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Wet oxidation of char–water-slurries from hydrothermal carbonization of paper and brewer's spent grains

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ABSTRACT

Char–water-slurries from the hydrothermal carbonization (HTC) of paper and brewer's spent grains at 200 °C or 240 °C were subjected to wet oxidation (WO) by gaseous oxygen at 170 °C or 200 °C without pre-separation into solid and water phases. The aim was to improve the heat efficiency of the HTC process while preferentially oxidizing the undesired dissolved organic matter (DOM) in the process waters over the chars. Success of this treatment was evaluated on the basis of the distribution of the feedstock chemical oxygen demand (COD) between chars and DOM. Results provide evidence that DOM and char underwent oxidation with a decrease in COD-to-carbon ratios. This fact could be attributed to changes in the concentrations of lactic, acetic, and formic acid quantified by ion chromatography. In oxidized process waters formic and acetic acids clearly dominate. Processes underlying the oxidation of chars are more diverse as revealed by FTIR spectroscopy and affect both cellulose-like and aromatic chars. A promising finding is that DOM was oxidized to a higher degree than the chars and that sufficient heat is released under certain WO conditions to thermally sustain the HTC process. Combined HTC/WO reaction regimes can be optimized for each specific biomass.

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1. Introduction

Methods of hydrothermal treatment are currently gaining importance for the energetic utilization of biomasses [1,2]. Hot compressed water is a cheap, sustainable and environmentally benign medium which solubilizes the polymeric components of the biomass and allows a range of chemical reactions, such as hydrolysis, dehydration, and depolymerization. Recently, considerable attention has been paid to hydrothermal carbonization (HTC) [3–5]. HTC is a conversion of both water-soluble and insoluble biomass into a solid coal-like material (the HTC char) and process water. The char has lignite-like characteristics, higher energy density and shows better dewaterability and chemical and biochemical stability than its feedstock. It can be used as fuel for conventional coal combustion facilities but also finds application as fertilizer and soil amendment [5]. Typical conditions for HTC are temperatures between 170 and 250 °C under elevated pressure (0.8–4.0 MPa) with residence times of one to several hours.

The HTC process is neither perfect in terms of solid carbon yield nor energetically self-sustainable despite some early predictions [3]. A considerable fraction of the feedstock carbon is always found as dissolved organic carbon (DOC) in the process waters (PWs) comprising both various classes of compounds of low molecular weight and macromolecular substances. Utilization and treatment of the PWs represent a challenging issue during HTC process engineering. The overall heat ($-\Delta H$) of the HTC reaction for example for cellulose conversion is rather low with 1.0 MJ kg^{-1} (dry basis) vs. the theoretical maximum of 2.4 MJ kg^{-1} due to the incomplete coalification process and side reactions [6,7].

A potential solution to both the problem of the elimination of DOC and the thermal self-sustainability of the process can be the post-application of a wet oxidation (WO) treatment [8,9]. HTC temperature and pressure framework are very similar to that of WO, a process that has been widely studied for removal of organic pollutants from wastewaters [10]. Partial WO has already been employed during the wet carbonization (i.e. HTC) of peat revealing that the oxidized chars showed better dewaterability but at the expense of higher solid carbon conversion to CO_2 even at mild conditions [11]. Two recent HTC-concepts suggest WO as post-treatment of HTC solutions using an excess of gaseous oxygen under similar pressures than during the HTC stage [12,13]. This can be achieved with a lower temperature during the WO stage compared to the HTC. The advantage of such a regime is the direct transfer of the hot HTC reaction mixture from the carbonization to the oxidation reactor. Heat transfer from the WO zone to the HTC reactor is expected to provide thermal self-sustainability.

There are two possible approaches to combine HTC with WO: (1) post-treatment of unseparated HTC slurries, i.e. mixtures of chars and PWs [11,13], and (2) separate treatment of PWs after filtration

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Abbreviations: BSG, brewer's spent grain; COD, chemical oxygen demand; DOC, dissolved organic carbon; DOM, dissolved organic matter; HTC, hydrothermal carbonization; POM, particulate organic matter; WO, wet oxidation.

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[12]. The latter strategy is free from a possible degradation of the chars through oxidation but more demanding in its engineering as HTC slurries need to be filtered, and thus the heat of the reaction mixture will be partly lost. The first approach could result in an undesired oxidation of the chars but the oxidation of HTC slurries is simpler from an engineering point of view. Furthermore, oxidizable organic pollutants present in HTC feedstocks from waste streams (e.g. sewage sludge) and odor-intensive substances, including those adsorbed on the char particles, would also be eliminated when HTC slurries are oxidized [14].

The aim of this paper is to prove the concept of the feasibility of the preferred oxidation of dissolved organic matter (DOM) components when unseparated HTC slurries are subjected to WO (Fig. 1). Two feedstocks are used: tissue paper as a model cellulosic biomass and brewer's spent grains (BSG). Gaseous oxygen is used as an oxidant under various temperature and pressure regimes. The objective is to find a combination of parameters for both the HTC and the oxidation stages that allows to (1) preferentially oxidize DOM, (2) spare the quality of the HTC char, and (3) oxidize DOM deeply enough to ensure an overall autothermal process regime. Since a complex network of chemical reactions proceeds under HTC and WO conditions, the heat of the reaction is difficult to calculate or obtain by direct measurements. Therefore, the heat of reactions will be estimated in an indirect way on the basis of the experimentally determined changes in chemical oxygen demand (COD) using the Thornton rule [15]. Furthermore, the higher heating value (HHV) can also be calculated according to Channiwala and Parikh on the basis of the elemental composition [16]. In the present study, rough estimations for the heat of reactions are sufficient, as it aims at a proof of principle if WO of HTC slurries can yield sufficient energy to sustain the HTC process without degradation of chars. This means that the goal is to find “mild” oxidation conditions to achieve a preferred oxidation of the DOM over the particulate organic matter (POM).

2. Materials and methods

2.1. Materials

Thick, coarse slurries (ca. 20 wt.% of solids) composed of commercially available unbleached tissue paper or BSG (Reudnitzer Brewery, Leipzig, Germany) were used in an acidic solution as HTC feedstocks. In case of paper, a 10 mM aqueous H_2SO_4 solution with 0.1 g L^{-1} of $FeSO_4$ were used as catalysts in HTC and WO reactions. In case of BSG, 100 mM aqueous H_2SO_4 solution was added to wet BSG (23 wt.% of solids) in a ratio of 1:7 (g/g) in order to obtain a pH of about 3. Additionally, several HTC experiments were carried out using paper in 1 mM aqueous H_2SO_4 solution as feedstock. If not otherwise specified, the “HTC of paper” will refer to the experiments with the acidic iron-doped reaction medium.

2.2. Experiments

HTC and WO experiments were carried out in in-house designed stainless steel autoclaves (internal volume 50 mL) with glass inserts (internal diameter 11 mm, length 22 cm) in which the biomass mixtures were placed. The sealed autoclaves were put into a preheated laboratory drying oven (200 °C or 240 °C for HTC experiments, 170 °C or 200 °C for WO) and held there for 4 h (HTC at 200 °C), 2 h (HTC at 240 °C), or 1 h (WO), respectively. After the desired reaction time, the autoclaves were cooled at room temperature and opened.

Oxygen for WO was generated in situ through the thermal decomposition of hydrogen peroxide as follows: After finishing the HTC stage of an experiment, the autoclaves were cooled, opened, and a measured amount of a 30 wt.% solution of H_2O_2 (Table S1) was put into the gap between the walls of the glass insert containing the HTC reaction mix and the steel autoclave. The autoclaves were sealed and placed for 1 h into the drying oven at 170 or 200 °C. The HTC chars were separated from the PWs by filtration and washed twice with distilled water. The wash waters were combined with the HTC process waters and filtered through 0.45 μm nylon syringe filters (Carl Roth GmbH, Germany). The combined water phases were used for PW characterizations. The HTC chars were dried at 105 °C for 16 h prior to analyses. All autoclave experiments were performed in duplicates or triplicates.

2.3. Analyses

The DOC content was determined after acidification of the PWs with 1 M aqueous H_2SO_4 solution and purging with N_2 using a total organic carbon analyzer TOC 600 (Shimadzu, Germany) in compliance with ISO 8245. The COD was determined using test kits (HACH LANGE GmbH, Germany). Titrations of acids were performed with 0.1 M aqueous NaOH solution until pH 12 was reached (automated titrator TitroLine, Schott-Geräte GmbH, Germany). Ion chromatography was performed on a Dionex ion chromatograph (DX500) equipped with an anion suppressor (ASRS300), conductivity detector (CD20) and an IonPac AS18 Anion-Exchange Column (4 × 250 mm) using a flow rate of 0.8 mL min^{-1} and gradient elution with the following program: 4 mM KOH from 0 to 7 min, increase to 40 mM KOH over 5 min, held for 10 min.

HTC chars were characterized by elemental analysis (C, H, N, S) using an automatic analyzer LECO model CHN 932 (LECO Instrumente GmbH, Germany) and FTIR spectroscopy pressed as tablets with KBr (System 2000 spectrophotometer, PerkinElmer). For the solids, the COD was calculated from stoichiometric considerations on the basis of the elemental composition. A correction for ash was made (ash determined by burning weighed samples in a tubular furnace at 900 °C).

In separate HTC experiments carried out in an autoclave with a headspace sampling port, the gaseous HTC products were analyzed for the presence of combustible gases (H_2, CO, CH_4) by gas chromatography using an Agilent 6850 gas chromatograph (Hewlett Packard) equipped with a molecular sieve column and a thermal conductivity detector.

3. Results and discussion

3.1. HTC and WO conditions

In the present work, two HTC regimes were used: 200 °C for 4 h and 240 °C for 2 h. The characteristics of feedstock and chars are summarized in Table 1. The more severe conditions allowed the production of

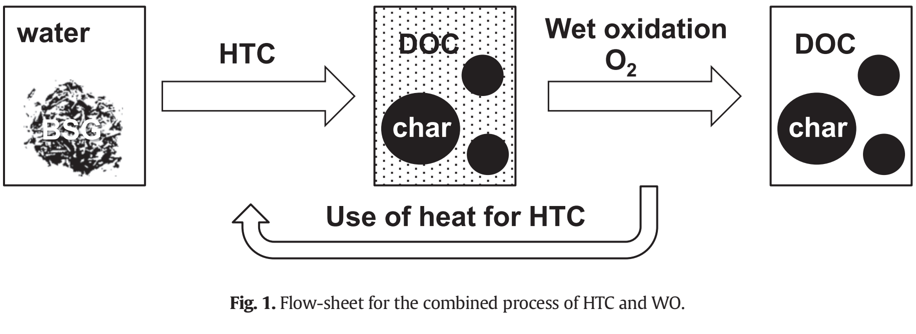

Fig. 1. Flow-sheet for the combined process of HTC and WO.

Table 1
Elemental composition and characteristics of the biomass feedstock and HTC-chars on a dry weight basis. The statistically determined uncertainties as relative standard deviations between replicates amounted to less than 2% (for paper) and less than 3% (for BSG and all HTC chars).

Feedstock	%C	%H	%N	%O	%S	g COD/g char	g COD/g char-C[a]	HHV [MJ·kg^{-1}] via Thornton	HHV [MJ·kg^{-1}] via Channiwala[b]
Paper	44.4	6.1	–	49.4	–	1.19	2.67	15.6	17.7
Paper HTC-char 200 °C, 4 h	54.8	5.7	–	39.5	–	1.52	2.78	20.1	21.8
Paper HTC-char 240 °C, 2 h	68.1	5.2	–	26.4	–	1.97	2.89	25.9	27.1
BSG	51.5	6.2	3.4	38.5	0.45	1.48	2.87	19.2	21.3
BSG HTC-char 200 °C, 4 h	63.8	5.8	2.9	27.1	0.40	1.87	2.94	24.7	26.3
BSG HTC-char 240 °C, 2 h	70.2	5.5	4.2	19.8	0.30	2.08	2.96	27.5	28.9

[a] COD/C [g COD/g char-C] = $(COD_{char} \cdot 100)/C$.
[b] HHV [MJ·kg^{-1}] = $0.3491 \cdot C + 1.178 \cdot H + 0.1005 \cdot S - 0.1034 \cdot O - 0.0151 \cdot N$.

chars with higher aromaticity and increased carbon content and HHV [17–19]. These "better quality" chars should be less susceptible towards oxidation. High concentrations of solids (20 wt.%) were chosen as HTC feedstock motivated by energetic considerations and the fact that this accelerates the carbonization reaction [20,21]. The influence of the concentration of solids, pH, residence time, and temperature on the outcome of the HTC reaction was already determined in earlier experiments [20,22].

HTC slurries produced at 200 °C were oxidized at 170 °C and those produced at 240 °C at temperatures of 170 °C and 200 °C, respectively. Thus, WO was always performed at lower temperatures than HTC in order to represent the engineering process [12,13]. Furthermore, WO temperatures lower than 200 °C should be able to spare particulate coals [11,12,4]. WO was performed at O_2 partial pressures of 0.5, 1.0, 1.5, and 2.0 MPa with a residence time of 1 h. This time was chosen to comply with the experimental set-up and to minimize oxidation of chars.

3.2. COD balance of HTC products after WO

The heat of reaction was determined indirectly via the COD using the Thornton rule [15]:

$$\mathrm{HHV} = \mathrm{COD} \times 13.2\ \mathrm{kJ\ g^{-1}}(\mathrm{oxygen}). \tag{1}$$

The difference between the amount of oxygen needed to completely oxidize the feedstock and the products (chars and PWs) will give the "free" COD, i.e. the released heat of the reaction. The COD of liquids was measured directly while the COD of solids was calculated from their elemental compositions. For a substance containing C, H, N, O and S (wt% from elemental analysis), assuming that its oxidation produces CO_2, H_2O, NH_3 and SO_2, the formal COD per grams over dry ash free basis was calculated as:

$$\begin{aligned}\mathrm{COD}\ &[\mathrm{g\ COD\ /\ g\ char}] \\ &= [(32/12) \times C + (16/2) \times H - (12/14) \times N + (32/32) \times S - O]/100.\end{aligned} \tag{2}$$

Assuming that inside the HTC plant there is an efficiency of heat exchange between input and output flows of about 60% and that 1 kg of water should be heated by 180 K from 20 °C to 200 °C for the HTC reaction (Eq. (3)), then additional 300 kJ per kg of water needs to be applied to sustain the HTC-process.

$$\mathrm{E} = \mathrm{m} \times \mathrm{c_p} \times \Delta\mathrm{T} \tag{3}$$

where m is the mass of water, c_P is the heating capacity of water (4.18 kJ kg^{-1} K^{-1} at 20 °C) and ΔT is the change in temperature. In order to gain these 300 kJ per kg of water, a fraction of the biomass feedstock can be oxidized: when cellulose with an HHV of 17.5 MJ kg^{-1} [23] is used as suspension with an organic dry matter content of 20 wt.%, then a complete oxidation of around 9% of the cellulose has to occur. When using BSG with an HHV of 22.3 MJ kg^{-1} (calculated according to Channiwala and Parikh [16]) at 20% organic dry matter conditions, 7% of BSG needs to be oxidized. For ease of calculations, 10% of biomass oxidation will be aimed at herein. Additionally, Prawisudha et al. reported that an energy content of 25% of the treated materials was required to sustain the HTC reaction [24]. Thus, oxidizing 25% of biomass will shortly be discussed herein as well.

The COD balance between feedstock and products of HTC (designated with 0 MPa of O_2) and WO was shown in Fig. 2a–c for paper and Fig. 3a–c for BSG, respectively. COD values for char and PWs were depicted as fraction of the feedstock COD. The difference between the sum of these two fractions and 100% was named "free COD" which can result from: (1) oxidation reactions, (2) formation of combustible gases (not quantitatively determined herein), and (3) balance losses. For WO experiments it was interpreted as a measure for the release of heat.

Only for low-temperature HTC of paper the COD balance was closed, i.e. no "free COD" was found (Fig. 2a). The high-temperature HTC of paper (Fig. 2b–c) and the HTC of BSG (Fig. 3a–c) exhibited considerable "COD losses" of up to 10% for paper and 18% for BSG. This indicated that combustible gases were formed during HTC. Qualitative analysis of the headspace in the autoclaves showed predominantly H_2 and CO formation [19,25].

If the "free COD" fraction of the HTC stage was taken as a base line for the reaction heat, it could be seen that under certain WO conditions additional 10% of the feedstock COD could be used to generate the desirable release of heat. This was the case for the combined reaction regimes of 200 °C-HTC and 170 °C-WO under high O_2-pressures of ≥1 MPa (Figs. 2a and 3a) and for 240 °C-HTC under either high O_2-pressures at 170 °C-WO (only for paper) or at 200 °C-WO (Figs. 2b–c and 3b–c). These regimes can be considered thermally self-sustainable. If a release of 25% of "free COD" was aimed at, only WO at high temperature of ≥1 MPa for paper and ≥2 MPa for BSG meet this criterion. However, the conversion of chars was significant under these conditions, the paper char-COD was reduced by almost 70% and BSG char-COD by 20%.

The HTC–WO-combinations could be optimized for conditions suitable to obtain thermal self-sustainability and at the same time having a minimum of char deterioration. However, the optimal regime had to be found for each biomass individually. BSG–HTC chars and waters had proven significantly more stable towards oxidation than those produced from paper. HTC chars of paper were especially labile during WO at 200 °C. Therefore, it was difficult to derive general rules for optimal HTC–WO parameter combinations from the two biomasses investigated in this study. Remarkably, 200 °C-HTC chars demonstrated a high resistance to WO similar to the 240 °C-HTC chars.

As indicators of the average oxidation state of the various organic matters, the gram-to-gram ratios of COD to mass of solids (g COD/g char), the COD to carbon content of chars (g COD/g char-C) and of PWs (g COD/g DOC) were shown for each regime (Figs. 2d–f and 3d–f). For example through stoichiometric considerations, the g COD/g

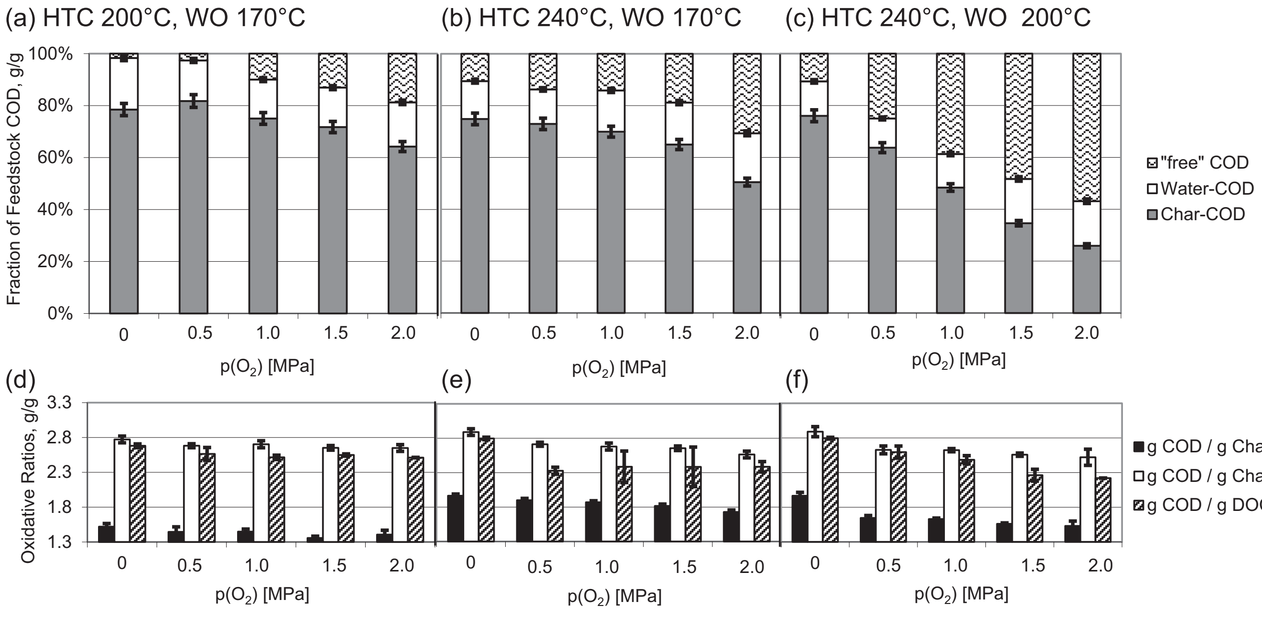

Fig. 2. Changes in COD and its distribution for different HTC–WO-combinations for paper as feedstock: in the upper row fractions of COD in chars, water and released "free" COD are referred to the total COD of the untreated feedstock; (a) HTC at 200 °C, WO at 170 °C; (b) HTC at 240 °C, WO at 170 °C; (c) HTC at 240 °C, WO at 200 °C. The lower rows show the ratios of COD to dry weight of the char (g/g), COD to carbon content of char, and COD to DOC of waters; (d) HTC at 200 °C, WO at 170 °C; (e) HTC at 240 °C, WO at 170 °C; (f) HTC at 240 °C, WO at 200 °C. The x-axes represent the O$_2$ partial pressure and 0 MPa refers to the intial HTC without WO.

char-C was calculated to be 2.67 for elemental carbon and carbohydrates, and the g COD/g char ratio was 2.67 for elemental carbon and 1.19 for cellulose (Table 1). The components of the DOM of untreated PWs (0 MPa) had a similar oxidation state as the chars produced at the same HTC regimes, i.e. they had COD-to-DOC ratios similar to the COD-to-carbon ratios of the chars [6,7,21].

A considerable amount of the COD (>10% of the feedstock COD) was always contained in the PWs, and no significant reduction of the COD in PWs was seen upon WO. POM tended to be oxidized along with DOM as seen from the decrease in char COD fractions with increasing O$_2$-pressures. This was most pronounced at high WO temperatures (Figs. 2a–c and 3a–c). A preferred oxidation of DOM vs. particulate char, seen as stronger decrease in the COD/DOC ratio compared to the COD to char-C ratio, could be achieved for the slurries from the 240 °C-HTC under certain O$_2$-pressures (Fig. 2 d–f and 3d–f).

Interestingly, the COD-to-char ratio decreased in a stronger way than the COD-to-C ratio (Figs. 2d–f and 3d–f). This could particularly be seen for WO of BSG–HTC slurries at 170 °C, under which conditions

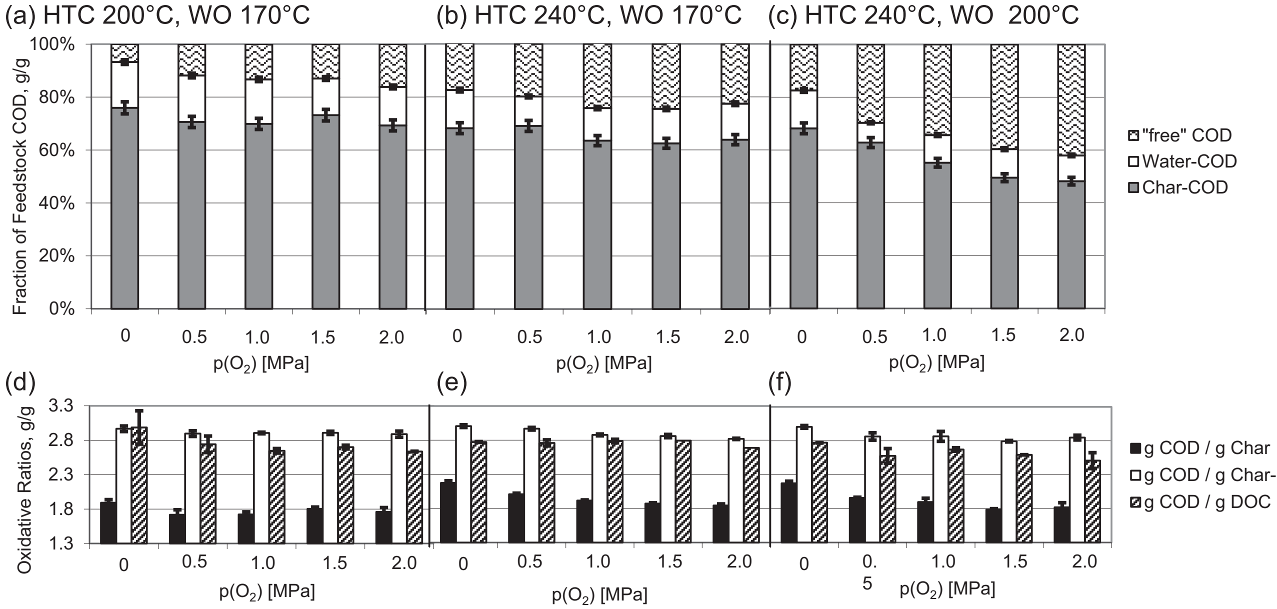

Fig. 3. Changes in COD and its distribution for different HTC–WO-combinations for BSG as feedstock: in the upper row fractions of COD in chars, water and "free" released COD are referred to the total COD of the untreated feedstock; (a) HTC at 200 °C, WO at 170 °C; (b) HTC at 240 °C, WO at 170 °C; (c) HTC at 240 °C, WO at 200 °C. The lower rows show the ratios of COD to dry weight of the char (g/g), COD to carbon content of char, and COD to DOC of waters; (d) HTC at 200 °C, WO at 170 °C; (e) HTC at 240 °C, WO at 170 °C; (f) HTC at 240 °C, WO at 200 °C. The x-axes represent the O$_2$ partial pressure and 0 MPa refers to the intial HTC without WO.

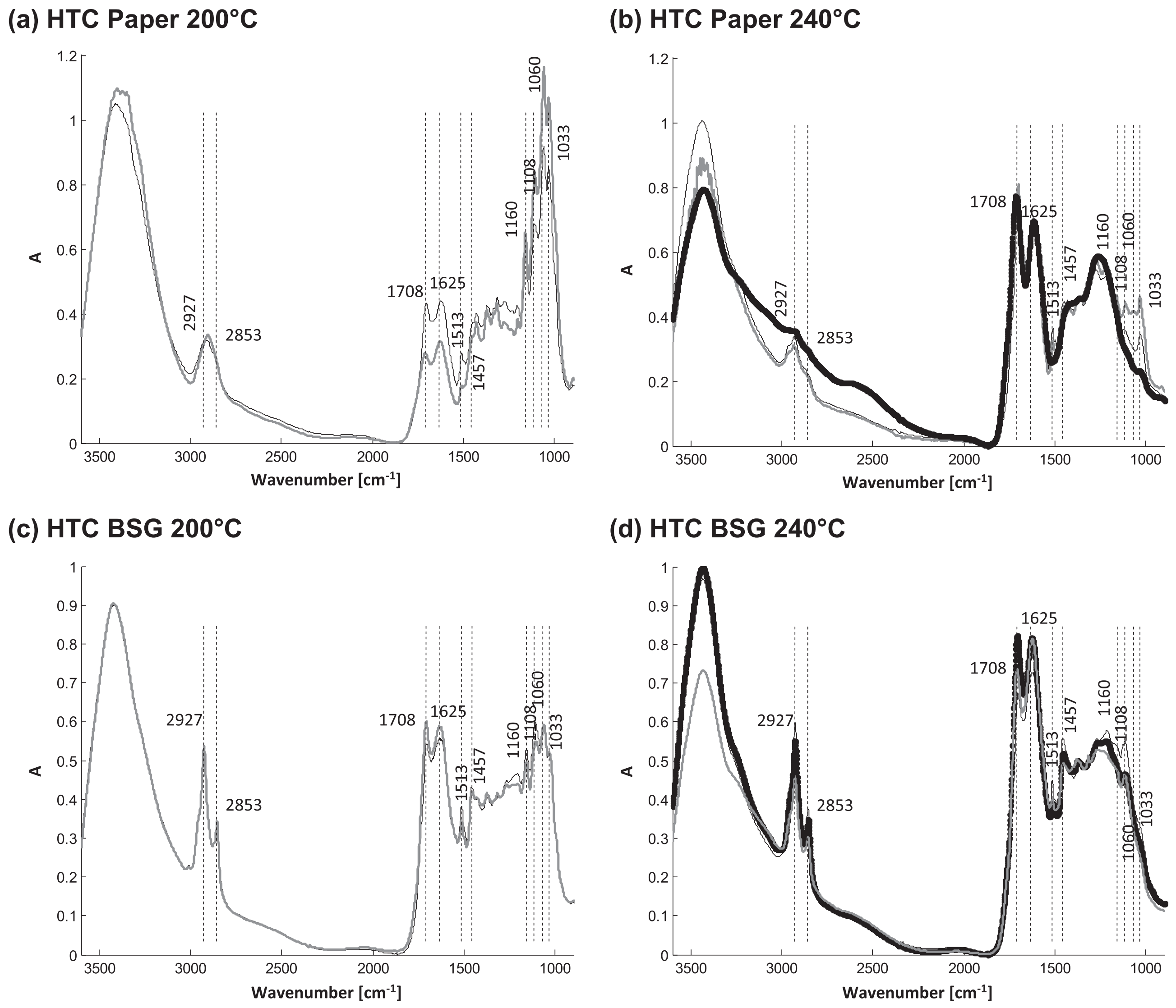

Fig. 4. FTIR spectra as area-normalized absorbance of dried HTC-chars (shown as thin black line) and WO products (shown as gray line for 1.0 or 2.0 MPa O_2 pressure at 170 °C, or bold line for 2.0 MPa O_2 pressure at 200 °C): (a) HTC of paper at 200 °C, WO at 1.0 MPa, 170 °C ; (b) HTC of paper at 240 °C, WO at 1.0 MPa, 170 °C, and 2.0 MPa, 200 °C; (c) HTC of BSG at 200 °C, WO at 2.0 MPa, 170 °C; (d) HTC of BSG at 240 °C, WO at 1.0 MPa, 170 °C, and 2.0 MPa, 200 °C.

the chars were relatively stable towards oxidation as hardly any decrease in the COD-to-C ratio was observed along with a decrease of the COD-to-char ratio. This indicated that hydrolysis (without changing the oxidation state of carbon) of char components prevails over oxidation. The char oxidation probably led to hydrolysable fragments that contribute to the DOM. The DOM was then oxidized to finally produce CO_2.

3.3. Infrared-spectroscopic investigation of HTC chars

FTIR spectra were recorded of HTC chars themselves and after WO to get a deeper insight into structural changes (Fig. 4). It could be seen that the coals from the 200 °C-HTC of paper possessed a very low degree of aromaticity (Fig. 4a). The spectra showed a distinctive pattern typical for carbohydrates (bands at 1033, 1060, 1112 and 1160 cm^{-1}), which means that the carbonization process had not been completed [17,18, 26,27]. Upon WO, only the relative intensity of the carbonyl bands had decreased (1625–1720 cm^{-1}). It could be suggested that an oxidative-hydrolytic cleavage of certain carbonyl moieties, which were most likely concentrated on the surface of the coal particles rather than in their core, occurred upon WO [17–19]. The cellulose moieties mostly resisted WO at 170 °C.

Chars from the 240 °C-HTC of paper (Fig. 4b) exhibited a higher degree of aromaticity and higher content of carbonyl groups compared to the 200 °C-HTC [17,18]. Their behavior upon WO at 170 °C was similar to that of the low-temperature chars, i.e. hydrolysis rather than oxidation might have occurred. Due to the absence of the initial cellulose fiber structure in these chars and less C–O–C linkages, the release of hydrolysable fractions into the DOM was proposed. At a WO temperature of 200 °C, destruction of C – C double bonds, C – H bonds and carbohydrate moieties can be seen while a high concentration of conjugated carbonyl moieties remained. Broadened signals of O – H stretchings suggest an increased formation of COOH-groups.

The FTIR-spectra of the BSG–HTC chars showed the presence of lignin features (Fig. 4c–d). Chars from both HTC temperatures were very similar [28]. Upon WO, no significant changes could be seen.

3.4. Oxidation behavior of the DOM

A large fraction of the DOM of the HTC PWs constitutes of short chain aliphatic acids, such as acetic, lactic and formic acid [6,22]. To evaluate the influence of WO on the formation and fate of acids, an additional series of HTC experiments at 240 °C was conducted using paper soaked in aqueous 1 mM H_2SO_4 solution to ensure nearly optimal HTC-

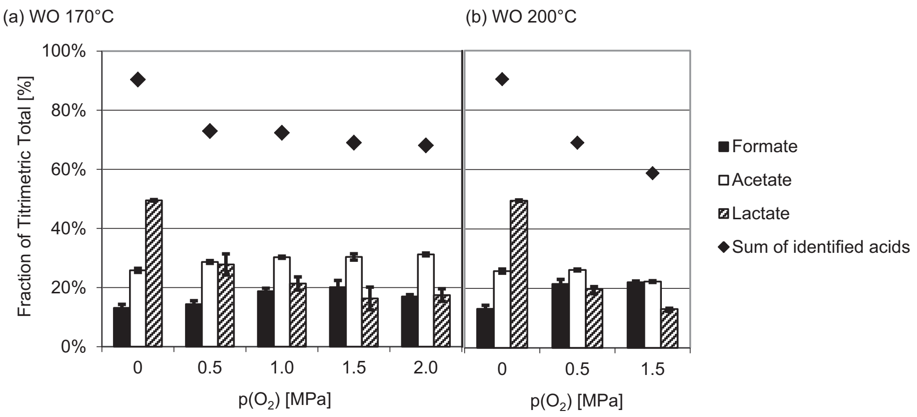

Fig. 5. The results of the ion chromatographic determination of selected organic acids (formate, acetate and lactate) in the PW after HTC at 240 °C in 1 mM aqueous H_2SO_4 solution and subsequent WO for paper as substrate: (a) WO at 170 °C, (b) WO at 200 °C. The concentrations are depicted as molar fractions of the total acid concentration determined by titration. Oxalate and propionate are included in the sum of identified acids, but not shown in the graph as their concentrations amount to <2% of total acids.

conditions by simultaneous minimization of the influence of inorganic ions on the analytical results. The PWs of HTC and WO were titrated against NaOH. One equivalence point at pH 7.5–8.0 is evident in the titration curve (see Supporting Information, Fig. S1). The dissolved organic carbon content per mol of hydroxide ions spent until the equivalence point decreased from 6 (70–80 g C/val acidity) in HTC PWs to 2.5 (30 g C/val acidity) after WO (see Supporting Information, Fig. S2). This reflects a decrease in the number of carbon atoms per mol of acid functionality. Thus, shorter chain acids seemed to dominate after WO. Ion chromatographic data showed the composition of the organic acids fraction with regard to the total acid concentration identified by titration in PWs of HTC (0 MPa) and WO of paper (Fig. 5). As expected, formic, acetic and lactic acids dominated this fraction. WO shifted the composition from lactate to acetate as the main component. The concentration of lactate decreased through oxidation while acetate remained relatively constant over varying oxidation conditions. The concentration of formate significantly increased, whereas oxalate and propionate amounted to <2% of the total acid concentrations (these were not depicted individually in Fig. 5, but only included in the sum of identified acids). The low concentration of oxalate in the oxidized waters is possibly due to its thermal instability under acidic conditions [29]. The sum of the determined carboxylic acids covered about 90% of the titrated acidity in the HTC PWs, but only 60 to 70% of those in the oxidized waters. Apparently, there were additional acidic compounds formed, which were not detected by the applied IC method. The organic carbon content of the detected acids amounted to about 30% of the DOC in the corresponding PWs irrespective of their origin. Thus, they were significant but not the dominant constituents in the WO waters.

These findings were in good agreement with the pathway proposed for direct WO of carbohydrates that had been described to result in the formation of formic acid [30]. Oxidation or oxidative hydrolysis of lactic acid produced acetic acid [30]. Both acetic and formic acids are relatively stable end products, as their oxidation is known to be relatively slow [9]. The increase in overall acidity upon oxidation seems to be promising to ensure a good biological degradability of the PWs. Thus, the oxidized DOM could be considered as a promising substrate for biogas production to further improve the overall energetic efficiency of combined processes.

4. Conclusions

The investigated combinations of HTC and WO of unseparated HTC slurries with focus on the COD balance did not show a considerable removal of DOC content in PWs, whereas the quality and amount of chars degraded. From the results presented herein it becomes evident that in order to fully spare the particulate matter from partial oxidation and maximize the yield of chars, the overall technological process should involve a hot filtration step. However, the DOM of the PWs from high-temperature HTC combined with WO exhibited a higher oxidation state than the particulate carbon. This is a positive finding that allows optimizing for a given biomass and a given HTC-regime the conditions under which the least amount of char is degraded. Most importantly, controlled WO proved to facilitate a thermally self-sustainable HTC if some losses in char yield could be accepted. This was the case for the combined reaction regimes of 200 °C-HTC and 170 °C-WO under high O_2-pressures of ≥ 1 MPa and for 240 °C-HTC and 200 °C-WO for both feedstock materials. All findings refer to experiments performed on very thick mixtures without intensive agitation. To what extent transport-controlled phenomena influence the results is subject to further research.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.fuproc.2014.07.042.

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